

A REDUCED GRAPHENE OXIDE ELECTRODE FOR SOLID-STATE HYDROGEN STORAGE WITHIN A PROTON BATTERY

HIMANSHU JINDAL¹, AMANDEEP SINGH OBEROI², INDERJEET SINGH SANDHU³
& MANSI CHITKARA⁴

^{1,3,4}Chitkara University Institute of Engineering and Technology, Chitkara University, Punjab, India

²Department of Mechanical Engineering, Thapar Institute of Engineering and Technology, Patiala, Punjab, India

ABSTRACT

Hydrogen may serve as sustainable eco-friendly and renewable energy resources, to meet challenges of climate change and decline of petroleum resources. Solid state hydrogen storage seems to be an appropriate method out of many more, due to high volumetric hydrogen energy density. In the present research work, the reduced graphene oxide synthesised, by chemical co-precipitation method, is explored as electrochemical hydrogen storage material. The novel organic concept employed for the synthesis of reduced graphene oxide using cedrusdeodara and fabrication of a solid electrode is reported. The fabricated electrode from the reduced graphene oxide has been tested in a reversible polymer electrolyte membrane fuel cell (PEMFC), what we have named as a 'proton battery', for solid-state hydrogen storage by galvanostatic charging and discharging. The electrochemical results of the electrode are analysed and discussed. In the present investigations, the electrochemical hydrogen storage capacity of cedrusdeodara reduced graphene oxide-based porous electrode integrated into a proton battery is found to be 1.44 wt. %. This Proton battery will have potential applications in the automotive industry and renewable energy sector.

KEYWORDS: Graphene, Reduced Graphene Oxide, Hydrogen Storage, Fuel Cell Application & Proton Battery

Received: May 14, 2019; **Accepted:** Jun 03, 2019; **Published:** Jul 06, 2019; **Paper Id.:** IJMPERDAUG201966

INTRODUCTION

The escalating population growth and rapid development of industrial sector have led to a continuous increase in energy demand[1]. Global energy consumption will become unavoidable at the current rate of consumption. The need for renewable energy resources has attracted tremendous attention throughout the world to prevent disasters caused by energy exhaustion[2]. In the global sustainable energy strategy, hydrogen can play a key role in addressing the twin challenges of climate change and decline of petroleum resources, both as transport fuel and long- term energy storage medium for power grids and other stationary power systems [3]. The specific energy content of hydrogen shows that hydrogen's chemical energy is about three times higher than of conventional fuels such as coal, gas, and oil[4]. It, is therefore, an ideal energy carrier for vehicle applications [5]. Hydrogen stored in solid-state is considered to be safer than other storage forms viz. liquid and gas[6]. In solid-state hydrogen is stored in the form of a chemical compound, known as electrochemical storage. However, energy stored per unit mass as well as volume of the storage medium differs in all these storage systems [7]. In liquid storage, one needs to maintain a temperature below 20 K and hence requires energy expenditure. Similarly, in the gaseous state, compressed hydrogen gas is stored in a pressurized vessel by spending energy to run the compressor, but compressed hydrogen gas system has low volumetric energy density as compared to liquid

hydrogen storage system [8]. Safety and storage cost are the main factors in the use of hydrogen as fuel [9]. In solid-state materials, hydrogen gets adsorbed physically and may include molecular hydrogen binding through weak Vander Waals forces called physisorption or generally stronger binding of atomic hydrogen called chemisorption creating a new compound [10]. Ideally, Solid state hydrogen storage materials should have the following features: rapid hydrogenation, dehydrogenation rates, high volumetric hydrogen energy densities and low temperatures for absorption and desorption [1]. Different carbon materials have been studied for solid-state hydrogen storage such as decorated graphene oxides, metal-organic framework, graphite nanofibers, and activated carbons [11].

Although lots of research has been carried out on carbon nanostructures for hydrogen storage, none of the materials could meet the U. S. DOE target of 5.5 wt. % of gravimetric energy density by 2020. The above-mentioned materials showed good hydrogen storage capacity. Graphene, a two-dimensional (2D) material with sp^2 honeycomb lattice-structured C atoms, has attracted considerable attention from researchers as a nanoscience technology material potential [12]. The unique mechanical, electrical, thermal and optical properties of this material are responsible for making it a most promising nanomaterial for solid-state hydrogen storage. The major challenge is to explore an effective graphene synthesis method. Various graphene production techniques, including mechanical exfoliation, chemical vapour deposition (CVD), chemical exfoliation, chemical synthesis, thermal chemical vapour deposition, unzipping nanotubes, microwave synthesis, pyrolysis and epitaxial growth have been applied [13]. Among these methods, the chemical reduction of graphene oxide is assumed to be the most efficient method for synthesizing soluble graphene at low cost in bulk quantities [14].

Usually, reducing agent such as hydrazine, hydrazine hydrate, dimethyl hydrazine, hydroquinone, hydrochloric acid, strong alkali, sodium borohydride and lithium aluminium hydride are used to convert graphene oxide into reduced graphene oxide (rGO) or grapheme [15]. The presence of traces of such toxic agents could lead to harmful effects on human health and a strong adverse impact on the ecosystem. Cedrus deodara is a very elegant ornamental tree found commonly on the western Himalayan hills. The Deodara tree in the Himalayas grows abundantly [16]. Cedrus deodara is an evergreen tree growing at a medium rate of 33 meters by 10 meters. It has a conical crown of horizontal branches and falling branches. The aqueous leaf extracts of cedrus deodara were used as a reduction and stabilizing agent for the synthesis of nanoparticle.

In the present investigations, the aim is to explore a novel green and facile strategy to produce reduced graphene oxide by reducing the graphene oxide in cedrus deodara solution. This approach is more suitable for large scale synthesis of soluble graphene for fuel cell applications because of distinctive features over other reported approaches. In addition, it is environment friendly approach because no synthetic chemical has been used in the reduction process and also hazardous waste is not generated during synthesis process. Moreover, it is simple, safe and cheap process. Therefore, the present work aims to produce sample cedrus deodara reduced graphene oxide, fabricate solid electrode from it and test the same in a proton battery, for electrochemical hydrogen storage.

EXPERIMENTAL

Materials and Chemicals

Graphite powder (100 microns, 150 mesh and Min 99.5 % particle size), potassium permanganate ($KMnO_4$), concentrated sulfuric acid (H_2SO_4) (98% extra pure), and hydrogen peroxide (H_2O_2) (30 %) has been procured from SD Fine Chemical Limited, Loba Chemie private limited, Merck, and Thermo Fisher Scientific Limited, Mumbai, India

respectively. The analytical graded chemicals, without further purifications, have been used in the present experiment and aqueous solution was prepared with deionised water. The reducing agent Cedrusdeodara leaves were collected from Almora, Uttrakhand, India.

Synthesis of Graphene Oxide (GO)

Graphene oxide was synthesised by Modified Hummer's method. The weighted quantity of graphite powder was added into a beaker containing 100 ml of H_2SO_4 and stirred with a magnetic stirrer at room temperature for 4 hours. Thereafter, 24g of potassium permanganate was slowly added into the above beaker and the temperature was maintained less than 20°C with gentle stirring. The solution was then heated up to 35°C in an electric oven for 2 hours. The resulting solution was diluted with 190 ml of distilled water and followed by stirring for 10 minutes. A dark brown suspension was obtained which was then heated at 98°C for 2 hours in an oven. Further dilution of the obtained solution was done by adding 400 ml of distilled water and continue stirring for 1hour. 40 ml of H_2O_2 30% concentration was added to the solution drop-by-drop while stirring. The excess of manganese salt was removed by washing graphene oxide suspension with 5% of hydrochloric acid (HCl) solution and thereafter filtration. The filtered contents were further washed with deionized water and filtration was done with $0.45\ \mu\text{m}$ paper till pH value of rinse water become neutral. Ultimately graphene oxide powders were obtained as shown in (Figure 1).



Figure 1: Graphene Oxide Powders

Reduction of Graphene Oxide by Cedrusdeodara (CD) Extract

Cedrusdeodara leaves weighed 50 g were washed with distilled water and grinded using domestic blender to obtain the slurry. The mixture was stirred well for about 15 minutes after adding 50 ml of distilled water. Further, the mixture was centrifuged at 1500 rpm for 15 minutes in order to make the suspended particles settle down. Finally, the extract was obtained by filtering the mixture with $0.45\ \mu\text{m}$ filter paper and filtrated was stored at 4°C . In order to obtain reduced graphene oxide, 5 ml of cedrusdeodara extract shown in (Figure. 2a) has been added in 100 ml of distilled water and the solution was sonicated at room temperature for 30 minutes. Further, 8 mg of reduced graphene oxide was added and the obtained solution was kept in an electric oven at 80°C for 4 hours. The final cedrusdeodara reduced graphene oxide (CD-rGO) was obtained in powdered form as shown in (Figure. 2b).

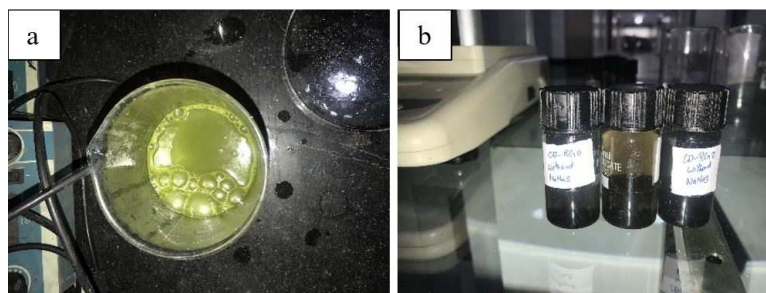


Figure 2: Reduced Graphene Oxide (a) Cedrusdeodara Extract, and (b) CD-rGO Powdered form

Electrode Fabrication

A weighted quantity of CD-rGO powder was mixed with polytetrafluoroethylene (PTFE) solution of 60 wt. % dispersion in H_2O . The role of PTFE solution is only to hold the CD-rGO particles together. The mixture was stirred in glass beaker in order to obtained slurry form. The slurry thus obtained has been poured into a die of the desired shape and a compressive load of 2 kg/cm² was applied on it with the help of a hydraulic press for 15 minutes. After 15 minutes, the die was removed from the press. The solid porous CD-rGO electrode was then removed from die as shown in (Figure. 3).

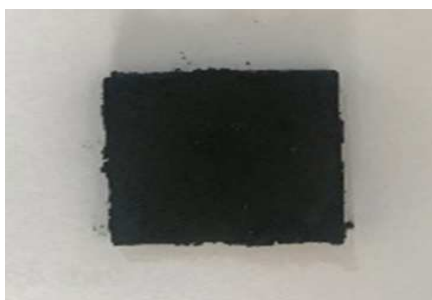


Figure 3: Cedrusdeodara Reduced Graphene Oxide Electrode (CD-rGO)

Fabrication of a Proton Battery

Fabrication of proton battery contains components as existing in usual unitized regenerative fuel cell (URFC). The components of proton battery are storage cylinders, bi-polar end plates, titanium frit, CD-rGO electrode, membrane electrode assembly (MEA), E-LAT hydrophilic carbon cloth and water supply tank. There are two bi-polar end plates in the proton battery one for hydrogen side (cathode) and another for oxygen side (anode). The hydrogen side end plate has parallel flow channels and two ports one for an exit of hydrogen gas and another for inlet, while battery is running on fuel cell mode in order to enhance the reaction rate. Similar flow channels were provided on the oxygen-side end plate along with three ports i. e. one for supply for water, second for oxygen gas outlet and third for oxygen gas inlet while proton battery running on fuel cell mode. A sintered titanium frit was employed as a gas diffusion layer on oxygen side to allow the diffusion of oxygen gases. Nafion-117 polymer, chemically known as perfluorosulfonic acid, is loaded with iridium ruthenium oxide and platinum black catalysts to form MEA. The catalyst loading on the oxygen side was 3.0 mg/cm² of Iridium ruthenium oxide and on the hydrogen side 3.0 mg/cm² of platinum black. The ELAT-hydrophilic plain carbon cloth was used as GDL on the hydrogen side end plate to allow the diffusion of hydrogen gases. Bi-polar plates were fastened by bolts and nuts to contain the fabricated CD-rGO electrode with specific surface area of 161.219 m²/g (Figure 4).

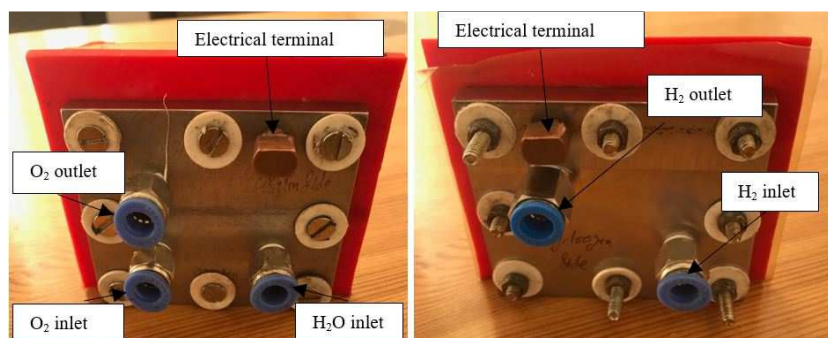


Figure 4: Oxygen Side Bi-Polar End Plate (Left) and Picture (Right) Hydrogen Side Bi-Polar End Plate of the Experimental Proton Battery System

CHARACTERIZATION

Morphology Characterization

The scanning electron microscopy (SEM) of the sample was obtained using JSM-6510LV at the Thapar Institute of Engineering and Technology, Patiala in India. This is done in order to find morphology of the microstructure of this material.

Electrochemical Measurements

For electrochemical measurements of CD-rGO electrode was employed in a proton battery which was charged by running it in electrolyser mode (E-mode) and discharged by running in fuel cell mode (FC-mode). During electrolyser mode or charging mode, the cell was supplied with distilled water and electric potential was applied across the cell. Under the influence of the applied voltage and catalyst loading on membrane electrode assembly (MEA), water dissociate into oxygen and hydrogen. Voltage was ramped up in equal increments and the corresponding results of current variation were recorded. Separate cylinders were used to collect the produced hydrogen and oxygen gases for later use. The cell was connected to variable load during FC- mode. The values of variations in current and voltage were noted, while load was varied. The proton battery under working condition is shown in (Figure. 5) with all necessary connections.

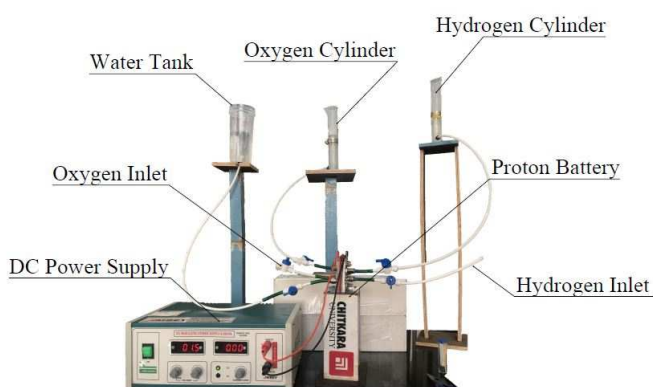


Figure 5: Proton Battery Set Up

Charge/Discharge Measurements

Galvanostatic charging /discharging was employed for electrochemical measurements to evaluate the CD-rGO electrochemical hydrogen storage capacity. The working of proton battery, i. e. under the applied electric potential the supplied water got disassociated under the influence of the catalysts present. The produced oxygen was allowed to move

out of the cell and collected in a graduated cylinder whereas; the hydrogen got further split into ions viz. protons and electrons. The produced H^+ ions pass through the polymer membrane (being a proton conductor allows H^+ to pass through) and e^- travels through the electric circuit. The H^+ ions emerging at ion exchange membrane combine with e^- and get adsorbed in the porous storage material (CD-rGO in this case) either physically or chemically or both. Ideally, H^+ shall get adsorbed without forming H_2 (hydrogen gas) however, some hydrogen gas does get liberated in the operation. The total hydrogen gas generated was calculated by using Faraday's law of charge conversation[17]. The hydrogen produced by the applied current in a particular time was calculated using:

$$m_{th} = \frac{It}{1000 \times F} \quad (1)$$

Where, ' m_{th} ' is the total hydrogen generated by the applied current in (g), ' I ' is charge/discharge current (mA), ' F ' is Faraday's constant (96485 J per volt gram) and ' t ' is the charge/discharge time (h)

RESULTS AND DISCUSSIONS

Morphology Characterization

The SEM images of graphene oxide and cedrusdeodara reduced graphene oxides sample prepared by novel green and facile strategy is shown in (Figure. 6). The recorded backscatters and secondary electron micrographs of CD-rGO show that well-developed pores are existing on the surface of graphene oxide. The comparison of micrographs of graphene oxide (Figure. 6a, 6b and 6c) and CD-rGO reveals that the structure of CD-rGO is more fibrous than GO. Hence CD-rGO is more suitable for hydrogen storage due to enhanced pores in its structures as shown in (Figure. 6d, 6e and 6f).

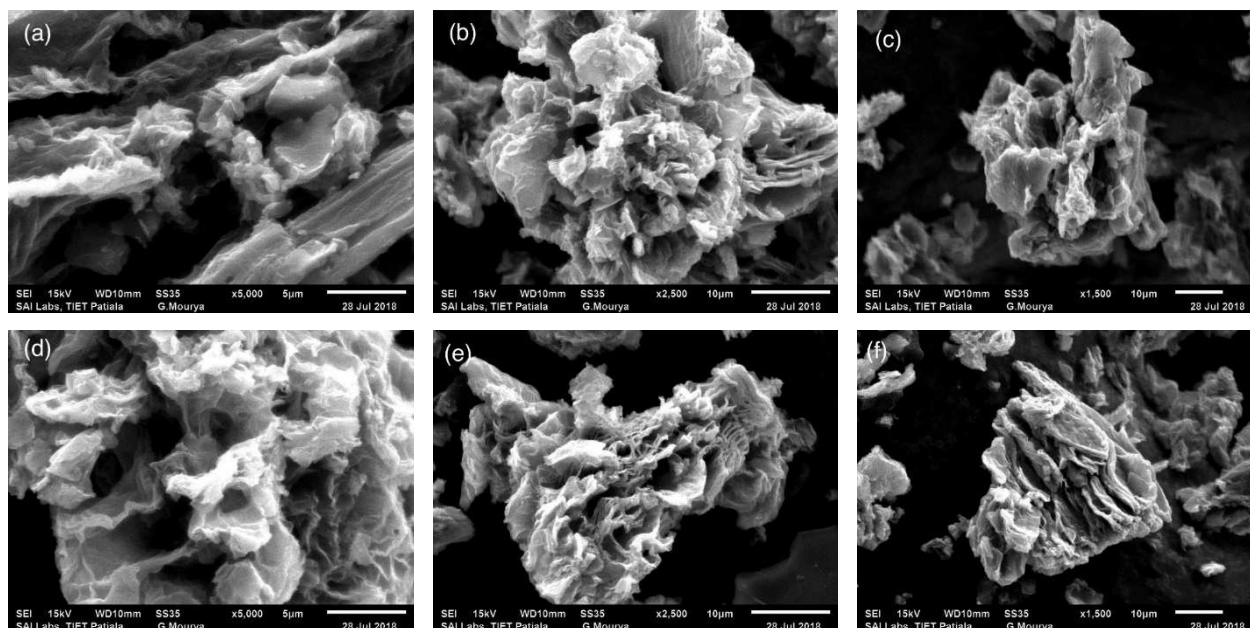


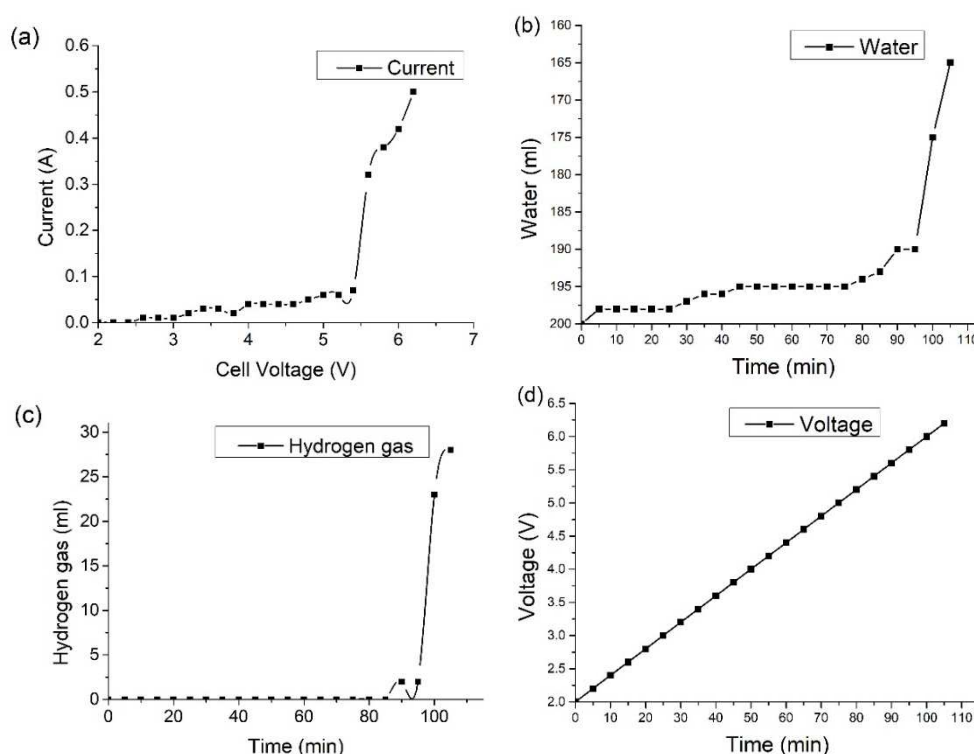
Figure 6: (a), (b) and (c) Scanning Electron Micrographs Images of Graphene oxide at Different Magnifications; (d), (e) and (f) Typical SEM Images of CD-rGO at Different Magnifications.

Hydrogen Storage Performance

Charging Results

The results as shown in (Figure. 7) were obtained when the proton battery, was charged using the electrical potential across the cell with voltage range between 2 and 6 V. The cut-in voltage, where the water disassociation was

observed to be started, was found to be 4.2 V. The proton battery was charged for 1.75 hours, until a rapid hydrogen gas production in the gas collection cylinder has been noticed. Initially, the low voltage was applied to cell to increase the probability of hydrogen entering the CD-rGO electrode and discourage hydrogen formation. Figure 7a shows the proton battery voltage vs current graph in E-mode or during charging. It could be seen that the V-I curve showed rather linear behaviour. It is to be noted that the curved plateau indicates the hydrogen adsorption in the storage electrode either chemically or physically[18]. Hydrogen ions (H^+) emerge in the chemical adsorption process at the electrolyte membrane, float over the acid (liquid proton conductor) and enter the carbon pores and which leads to formation of weak chemical bonds on its inner surface of carbon pores. In the physical adsorption process, H^+ ions are physically withheld in micro pores (diameter less than 0.7 nm) of graphene under the influence of Vander Waals forces.



**Figure 7: (a) Cell Voltage vs Current Behaviour During Charging;
(b) Water Consumption with Time when Proton Battery was Run in E-Mode;
(c) Hydrogen Gas Production Behaviour vs Time;
(d) Cell Voltage vs Time Behaviour During Charging**

The operation was stopped when the rapid generation of gas bubbles in the gas collection cylinders were observed, indicating that the storage is complete and all the produced H ions are combining with electrons to form hydrogen gas instead of electrochemical adsorption. In E-mode, the water was supplied continuously to the cell and hydrogen protons (H -protons) get emerged on the membrane. The consumption of water was recorded as shown a graph in Figure. 7b. The decrease in water level is obvious because of the dissociation. This sharp downfall is in correspondence with the sudden increase in the formation of hydrogen gas. This is due to higher catalytic loading on MEA with iridium ruthenium oxide of $3\text{mg}/\text{cm}^2$ of and platinum black of $3\text{mg}/\text{cm}^2$. The gas liberation is shown in Figure. 7c. The proton battery has more oxygen release due to a higher amount of platinum black that improves the reaction of water dissociation. This is because the proton battery is charged by hydrogen storage through the adsorption process in the storage electrode (Figure.7d) shows that a gradual increase in voltage begins at 2 V up to a maximum of 6.2 V. Storage electrode contains

porous surface where the hydrogen H^+ ions are stored to be used in the future for fuel cell mode. Table 1 shows the parameters obtained during charging of proton battery. The mass of hydrogen produced in different stages is described with the respective equations in Table 2.

Table 1: Parameters during Charging of Proton Battery

Parameters during Charging	Value Obtained during Charging in Reduced Graphene Oxide
Volume of hydrogen gas generated (V)	28 cm ³
Current during charging (I)	500 mA
Time of charging (h)	1.75 h
Mass of cedrusdeodara reduced graphene oxide (m_c)	0.457 g
Total mass of electrode (m_e)	0.655 g

Table 2: Mass of Hydrogen Produced in Different Stages

Parameters	Equations	Value Obtained During Charging in Reduced Graphene Oxide
Mass of total hydrogen generated (m_{th})	$\frac{It}{1000 \times F}$	0.03264 g
Mass of hydrogen gas produced (m_{hg})	$\frac{PV}{RT}$	0.002328 g
Mass of hydrogen stored electrochemically (m_{he})	$m_{th} - m_{hg}$	0.030312 g
Total mass of hydrogen produced	$\frac{100 \times m_{th}}{m_c}$	7.14 wt. %
Mass of hydrogen entering to the electrode	$\frac{100 \times m_{he}}{m_c}$	6.63 wt. %

Where, 'P' is absolute pressure of the gas (Pa), 'V' is the volume of gas (cm³), 'R' is universal gas constant (8.314 J/kg K) and 'T' is absolute temperature (K)

Discharging Results

The cell was connected to an electric load in FC mode or during the process of discharge. The discharge current time was recorded. The current and time characteristics over time are shown below in (Figure.8). Under the influence of the electrical load, the weak chemical bonds of hydrogen atom with carbon break-up and hydrogen atom come out of the storage. The catalyst loading splits the hydrogen atom back into H^+ and e^- . H^+ ions return back to cathode through polymer electrolyte membrane and e^- travels through wires giving out electricity. At cathode, oxygen produced during charging is supplied back that reacts with H^+ and e^- to reform water. It is to be noted that there is no other source of hydrogen power generation but, the hydrogen stored electrochemically in the reduced graphene oxide electrode. Also, after connecting to an electrical load we observe decrease in the reading of current. This is due to the decrease in the supply of hydrogen ions from CD-rGO electrode. Table 3 shows the discharging parameters obtained during discharging of proton battery. The amount of hydrogen gas released during discharging as shown in Table 4.

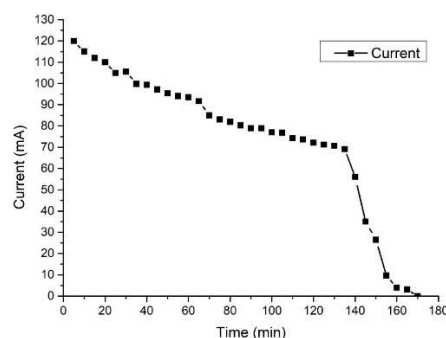


Figure 8: Current vs Time Graph of the Proton Battery

Table 2: Parameters during Discharging of Proton Battery

Parameters during Discharging	Value Obtained during Discharging in Reduced Graphene Oxide
Current during discharging (I)	120 mA
Time of charging (h)	1.5 h
Mass of cedrusdeodara reduced graphene oxide (m_c)	0.457 g
Total mass of electrode (m_e)	0.655 g

Table 4: Mass of Hydrogen Released During Discharging

Parameters	Equations	Graphene Electrode
Mass of hydrogen stored electrochemically and release during discharging (m_s)	$\frac{It}{1000 \times F}$	0.06716 g
Mass % of hydrogen released in electrode	$\frac{100 \times m_s}{m_s + m_e}$	1.01 wt. %
Mass % of hydrogen released in reduced graphene oxide	$\frac{100 \times m_s}{m_s + m_c}$	1.44 t. %

CONCLUSIONS

The graphene oxide material has been synthesised using Modified Hummers Method. The reduced graphene oxide is obtained from synthesised graphene oxide using a natural reducing agent - cedrusdeodara extract. It has been observed that reduced graphene oxide is more porous as compared to graphene oxide and therefore is more suitable for electrochemical hydrogen storage because it possesses high volume of ultra-micropores (having diameter $< 0.7\text{nm}$) which are considered as active sites for electrochemical hydrogen storage. The electrode was fabricated from CD-rGO and electrode was tested using proton battery. The charging and discharging capacity of electrodes has been measured. It is successfully shown that hydrogen can get adsorbed electrochemically in porous CD-rGO and come out to generate electricity. The electrochemical hydrogen storage capacity obtained is 1.44 wt.%. The results have demonstrated the technical feasibility of proton battery with an integrated CD-rGO based hydrogen storage electrode with potential applications in the field of automotive industry and energy storage for remote area power supply. However, further work is required to be done in surface morphology of CD-rGO to understand better its effect on electrochemical hydrogen storage. Other liquid conducting mediums like such as protic ionic liquids and conducting gels might be tested in future to obtain improved gravimetric and volumetric energy storage density. Future scope work would also include the rapid cyclic testing of the developed proton battery to disclose its durability. It is surely a step forward towards meeting the U. S. DOE goal for hydrogen storage by 2020 and contribution towards a sustainable society.

REFERENCES

1. N. Rusman and D. M., "A review on the current progress of metal hydrides material for solid-state hydrogen storage applications," *International Journal of Hydrogen Energy*, vol. 41, no. 28, pp. 12108-12126, 2016.
2. C. Hyun-Jung, J. Sun-Min, S. Jeong-Min, C. Dong Wook, D. Liming and B. Jong-Beom, "Graphene for energy conversion and storage in fuel cells and supercapacitors," *Nano Energy*, vol. 1, no. 4, pp. 534-551, 2012.
3. A. John and S. M. Saeed, "Towards a 'proton flow battery': investigation of a reversible PEM fuel cell with integrated metal-hydride hydrogen storage," *International Journal of Hydrogen Energy*, vol. 39, no. 4, pp. 1740-1751, 2014.
4. T. Sadhasivam, H. T. Kim, S. Jung, S. H. Roh, J. H. Park and H. Y. Jung, "Dimensional effects of nanostructured Mg/MgH₂ for hydrogen storage applications: A review," *Renewable and Sustainable Energy Reviews*, vol. 72, pp. 523-534, 2017.
5. N. A. Sazelee, N. H. Idris, M. F. Md Din, N. S. Mustafa, N. A. Ali, M. S. Yahya, F. A. Halim Yap, N. N. Sulaiman and M. Ismail, "Synthesis of BaFe₁₂O₁₉ by solid state method and its effect on hydrogen storage properties of MgH₂," *International Journal of Hydrogen Energy*, vol. 43, no. 45, pp. 20853-20860, 2018.
6. Singh, A. N. A. N. D., & Baredar, P. R. A. S. H. A. N. T. (2016). A technical, economic, and environmental performance of hybrid (solar-biomass/fuel cell) energy system. *International Journal of Environment, Ecology, Family and Urban Studies (IJEEFUS)*, 6(5), 17-26.
7. S. S. Murthy, "Report on hydrogen storage and applications other than transportation," Ministry of New and Renewable Energy, Government of India, New Delhi, 2016.
8. A. S. Oberoi, "Hydrogen storage capacity of selected activated carbon electrodes made from brown coal," *International Journal of Hydrogen Energy*, vol. 41, no. 48, pp. 23099-23108, 2016.
9. A. Zuttel, "Materials for hydrogen storage," *Materials Today*, vol. 6, no. 9, pp. 24-33, 2003.
10. Y. Honarpazhouh, F. R. Astaraei, H. R. Naderi and O. Tavakoli, "Electrochemical hydrogen storage in Pd-coated porous silicon/graphene oxide," *International Journal of Hydrogen Energy*, vol. 41, no. 28, pp. 12175-12182, 2016.
11. V. d. Berg, A. W. and C. O. Arean, "Materials for hydrogen storage: Current research trends and perspectives," *Chemical Communications*, vol. 6, pp. 668-681, 2008.
12. S. Konstantinos, D. Gournis and P. Rudolf, "Hydrogen storage in graphene-based materials: efforts towards enhanced hydrogen absorption," *ECS Journal of Solid State Science and Technology*, vol. 2, no. 10, pp. M3160-M3169, 2013.
13. D. Hou, Q. Liu, H. Cheng, K. Li, D. Wang and H. Zhang, "Chrysanthemum extract assisted green reduction of graphene oxide," *Materials Chemistry and Physics*, vol. 183, pp. 76-82, 2016.
14. S. W. Chong, C. W. Lai and S. B. A. Hamid, "Green preparation of reduced graphene oxide using a natural reducing agent," *Ceramic International*, vol. 41, no. 8, pp. 9505-9513, 2015.
15. R. B. Mathur, B. P. Singh and S. Pande, *Carbon nanomaterials: synthesis, structure, properties and applications*, Boca Raton: Taylor & Francis, 2016.
16. C. S. R. Vusa, S. Berchmans and S. Alwarappan, "Facile and green synthesis of graphene," *RSC Advances*, vol. 4, no. 43, pp. 22470-22475, 2014.
17. H. I. Borgaonkar, G. B. Pant and K. R. Kumar, "RING-WIDTH VARIATIONS IN Cedrus deodara AND ITS CLIMATIC," *International Journal of Climatology*, vol. 16, no. 12, pp. 1409-1422, 1996.

18. K. L. Lim, H. Kazemian, Z. Yaakob and W. W. Daud, "Solid-state materials and methods for hydrogen storage: a critical review," *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, vol. 33, no. 2, pp. 213-226, 2010.
19. K. Jurewicz, E. Frackowiak and F. Beguin, "Towards the mechanism of electrochemical hydrogen storage in nanostructured carbon materials," *Applied Physics A*, vol. 78, no. 7, pp. 981-987, 2004.

